In situ Raman Spectroscopic Study of Oxygen Adspecies on a Th-La-O_x Catalyst for Methane Oxidative Coupling Reaction

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The superoxide adspecies O_2^- is identified by *in situ* Raman spectroscopy on a functioning Th–La–O_x catalyst for methane oxidative coupling reaction at 680–860 °C.

Methane oxidative coupling (MOC) has the potential to form ethane and ethene from natural gas and a large number of catalysts for the reaction have been reported. The oxygen species such as O_2^-, O_2^{2-} and O^- involved on catalyst surfaces responsible for the initial methane activation step is of great interest.[1–6] To gain further insight into the nature of the surface oxygen species and their role in the activation of methane, *in situ* spectroscopic study at the actual reaction conditions is more helpful. Recently, peroxide adspecies O_2^{2-} was reported to be identified *in situ* on La_2O_3, Na^+-La_2O_3, Sr^{2+}-La_2O_3 and Ba^{2+}-MgO catalysts.[7,8] In the present work, *in situ* laser Raman spectroscopy has been used to characterize the surface oxygen species on a working Th-La-O_x MOC catalyst at 680–860 °C.

The Th-La-O_x (Th : La = 10 : 1.5, mol ratio) catalyst was prepared by drying (160 °C, 10 h) and calcination (880 °C, 4 h) of a freshly coprecipitated mixture of carbonate and hydroxide. The Th-La-O_x was a very active catalyst for the MOC reaction. Under cofeed reaction conditions of $CH_4/O_2 = 4/1$ (mol ratio), GHSV = 6.0×10^4 h^{-1}, atmospheric pressure and 740 °C, a C_2-hydrocarbons yield of 14.6% with C_2-hydrocarbons selectivity of 55.8% was obtained over the catalyst.

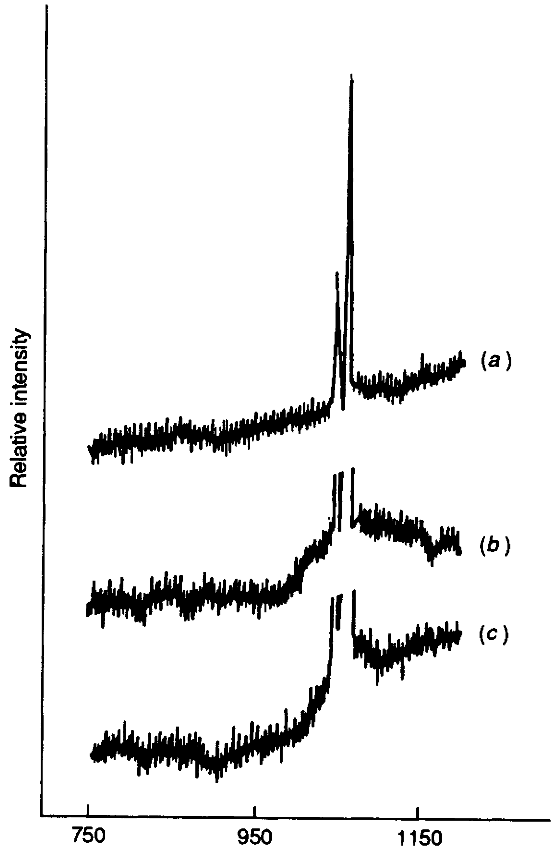

Fig. 1 *In situ* Raman spectra of the Th-La-O_x catalyst at 740 °C. (*a*) Spectrum taken 1 h after switching the gas flow from CH_4/O_2 (4 : 1, mol ratio) to O_2. (*b*) In a gas flow of CO_2. (*c*) In a gas flow of $CO_2/H_2O(g)$ (92 : 8 mol ratio).

Raman spectra were recorded using a Jobin-Yvon U-1000 Raman spectrometer with argon laser (488.0 nm line, 200 mW) as excitation source; slit width settings corresponded to a resolution of 4 cm^{-1} and 36 scans were accumulated. A high temperature controlled-atmosphere cell[9] was used to obtain *in situ* spectra on the working Th-La-O_x catalyst; the particle size

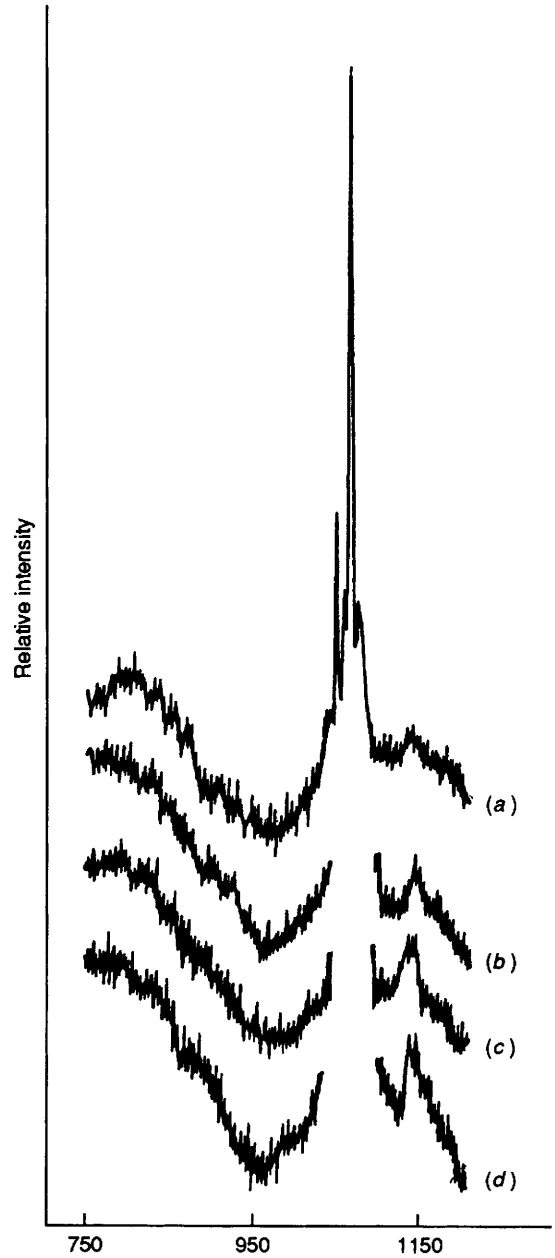

Fig. 2 *In situ* Raman spectra of the working Th-La-O_x MOC catalyst in a stream of CH_4/O_2 (4 : 1, mol ratio) mixture with total gas flow rate of 150 ml min^{-1}, at 1 atm. and the reaction temperature of (*a*) 860 °C, (*b*) 800 °C, (*c*) 740 °C and (*d*) 680 °C

of the catalyst sample being 50–80 mesh and weight about 1.0 g.

Fig. 1(*a*) shows the *in situ* Raman spectrum of the Th-La-O_x at 740 °C in a flow of O_2 taken 1 h after switching the gas flow from CH_4/O_2 (4/1) mixture. A pair of bands at 1060 and 1046 cm^{-1} were clearly observed. These bands can be assigned to surface carbonate species CO_3^{2-}.[10] It is noteworthy that no band assignable to dioxygen adspecies was observed under these conditions.

CO_2 and H_2O are the products of the MOC reaction. To test whether adsorption of CO_2 and H_2O on the Th-La-O_x may cause the assignment confused with the Raman band of dioxygen adspecies, a spectrum was recorded when the sample was treated in a flow of CO_2 or $CO_2/H_2O(g)$, respectively. The results show that the adsorption of CO_2 or $CO_2/H_2O(g)$ only cause the increasing band intensity of CO_3^{2-}.

Fig. 2 exhibits a series of *in situ* spectra of the working Th-La-O_x catalyst at reaction temperatures of 860, 800, 740 and 680 °C, respectively, under cofeed MOC reaction conditions. Raman bands which can be clearly resolved are those at 1060, 1046 and 1140 cm^{-1}. The very strong bands at 1060 and 1046 cm^{-1} together with a number of shoulders on these bands are attributed to surface carbonate species CO_3^{2-} [shown only in Fig. 2(*a*)]. The band observed at 1140 cm^{-1} can be ascribed to the O–O stretching mode for superoxide species O_2^- on the surface of the Th-La-O_x catalyst. This band position is consistent with those of superoxide adspecies observed on other oxides,[11–13] and with those of the superoxide ligand reported in the matrixes and complexes.[14] It can be clearly observed that the relative intensity of the Raman band at 1140 cm^{-1} increased with decreasing reaction temperature. The intensity of the 1140 cm^{-1} band was also found to enhance with increasing O_2 concentration in the feed.

Generally speaking, adsorbed oxygen species transform on the surface of metal oxide catalysts according to eqn. (1).[15,16]

$$O_2 \rightleftharpoons \underline{O_2} \xrightarrow{e} \underline{O_2^-} \xrightarrow{e} \underline{O_2^{2-}} \rightarrow \underline{2O^-} \xrightarrow{2e} \underline{2O^{2-}} \text{ (lattice)} \qquad (1)$$

(an underlined chemical species signifies a chemisorbed or surface species)

O_2^- adspecies may form from a chemisorbed O_2 by acquiring an electron from the metal oxide. The reason that no Raman band of dioxygen adspecies was observed in Fig. 1(*a*) may be that the charged dioxygen adspecies could not be formed easily on the Th-La-O_x surface due to weak electron donation of the surface under this condition—CH_4-free flowing O_2-stream. This result is consistent with the work of C. Li *et al.* They found that no IR signal corresponding to O_2^{2-} or O_2^- adspecies on cerium oxide could be detected at the temperature of 420 K under the pure O_2 atmosphere.[13]. However, when CH_4 was cofed with O_2 to pass the catalyst, the catalyst surface may be partially reduced by CH_4, then adsorbed O_2 can gain an electron easily from the surface and transform into O_2^- adspecies. It has been reported that O_2^- was able to activate methane at the MOC reaction temperature.[4,17] Thus, the O_2^- formed primarily may subsequently take part in methane activation step or transform further to O_2^{2-} adspecies *via* gaining an electron again from the surface. The results of the present work also indicate that, under the reaction temperature between 680 and 880 °C, the steady concentration of O_2^{2-} species, whose Raman signal is usually expected to appear in the region of 750–900 cm^{-1}, on the surface of functioning Th-La-O_x MOC catalyst is below the detectable limit of the Raman spectroscopy.

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